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(21) International Application Number: PCT/AU98/00611 (22) International Filing Date: 3 August 1998 (03.08.98) (30) Priority Data: PO 8401 4 August 1997 (04.08.97) AU (71) Applicant: BARRY CROMMELIN NOMINEES PTY. LTD. [AU/AU]; 72 Division Street, Welshpool, W.A. 6106 (AU). (72) Inventors: FEHERVARY, Alexander (deceased).CLARK, William; 151 Timberlane Drive, Woodvale, W.A. 6026 (AU). (74) Agents: HARWOOD, Errol, John et al.; Wray & Associates, 239 Adelaide Terrace, Perth, W.A. 6000 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: SELF-CURING COMPOSITION (57) Abstract The present invention relates to a self-curing composition for a polymeric composition comprising (a) a silicon containing compound or a salt limited solubility; (b) an oil, an olefine or a fatty acid; and (c) a starch, a carbohydrate, a polysaccharide, a cellulose or a gum. The self-curing composition preferably comprises a thermoplastic polymer or any anionic emulsion of a thermoplastic which is unstable in combination with small amounts of a cation. The present invention also relates to a method of controlling the curing of a thermoplastic polymer.		

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TITLE: "Self-Curing Composition"**BACKGROUND OF THE INVENTION**

The present invention relates to a self curing polymeric composition. In particular, the present invention relates to a self curing polymeric composition for
5 rubber compositions.

Self curing polymeric compositions are known whereby an agent present in the composition reacts at ambient temperature to form a cured or crosslinked polymer. These self curing polymeric compositions have a variety of applications comprising use as waterproof membranes, adhesives, paints and lacquers.

10 A problem or disadvantage that exists with known self curing polymeric compositions is that under conditions with high humidity and/or low temperature or with poor air movement, the agents present in the composition do not allow at ambient temperature the formation of a cured or crosslinked polymeric product.

Throughout the specification, the term "cured" will include partially cured
15 polymeric products which resist deformation on application of force as applied by a thumb test. The term "cured" will also include fully cured and substantially cured polymeric products.

In particular, self curing polymeric compositions which delay the curing over an extended period of time, for example 24 to 48 hours, suffer from the problem of
20 not curing at ambient temperature to form the cured polymeric product.

SUMMARY OF THE INVENTION

It is an object of the present invention to seek to overcome or, at least, reduce the above stated problems with the prior art.

According to a first aspect of the present invention, there is provided a self curing
25 composition for a polymeric composition comprising

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- (a) a silicon containing compound or a salt with limited solubility,
- (b) an oil, an olefine or a fatty acid; and
- (c) a starch, a carbohydrate, a polysaccharide, a cellulose or a gum.

5 The composition preferably has the oil such that it has a medium saponification number. The oil may be a naphthenic or process oil. The oil may also be in the form of a vegetable oil. The vegetable oils include cottonseed, peanut, rapeseed, sunflower, canola oil and safflower oil

In a preferred form, the starch is a cold water swellable and soluble starch. The starch is preferably in the form of a corn starch.

10 The composition also preferably includes water.

The silicon containing compound is preferably a halogen containing compound. The silicon containing compound which contains halogen preferably includes fluorine containing and chlorine containing compounds. In particular, the preferred halogen containing silicon compounds include alkali silico halides.

15 The composition also preferably includes a biocide to provide antifungal properties to the composition.

According to a second aspect of the present invention, there is provided a self curing polymeric composition comprising

- (a) a thermoplastic polymer;
- 20 (b) a self curing composition comprising a silicon containing compound, an oil and a starch.

According to a third aspect of the present invention, there is provided a method of controlling the curing of a thermoplastic polymer comprising the steps of

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a) premixing a starch, an oil and a curing agent in an aqueous solution to form a coated curing agent;

b) adding the coated curing agent to the thermoplastic polymer;

such that thermoplastic polymer will be cured over an extended period of time.

5 DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic polymer is preferably a polychloroprene polymer, bituminous polymer, asphaltic polymer or any anionic emulsion of a thermoplastic polymer which is unstable in combination with small amounts of a cation.

Other suitable polymers include acrylic resins, polyurethanes,
10 Styrene/Butadiene/Rubber (SBR) resins, polyvinyl acetate resins, synthetic rubber resins and polyethylenes and polyvinyl chloride resins.

In accordance with one embodiment of the present invention, the self curing polymeric composition is a controlled release self curing composition which operates such that curing of the polymer will occur after a predetermined time.

15 The predetermined time is preferably in the range of half an hour to 8 hours.

The self curing composition according to a preferred aspect of the present invention is a composition which when added to a thermoplastic polymer will not immediately cure or cross link the thermoplastic polymer. Rather, the oil, the starch and the silicon containing compound are pre-mixed in a manner so as to
20 allow the curing or cross linking of the thermoplastic polymer to be controlled or delayed over an extended period of time.

It is believed that the starch and oil act to form a coating over the silicon containing compound which is thought to act to cure or cross link the thermoplastic polymer. Since the silicon containing compound is coated with the
25 oil and starch, it is believed that the curing or crosslinking reaction of the

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thermoplastic polymer and the curing agent is delayed. The adjustment of the ratios of the oil, starch and the silicon containing compound can control the rate of release of the curing agent to the thermoplastic polymer. However, it is to be understood that the components of the self curing composition may operate in another manner to that just described.

The components in the self curing composition comprising starch, the silicon containing compound and the oil are mixed in such a ratio so as to provide curing or crosslinking of a thermoplastic polymer under conditions of high humidity and/or low temperature.

10 A preferred range for the starch is 300 to 450 parts. A further preferred range for the starch is 320 to 420 parts. A still further preferred range is 350 to 400 parts. A yet still further preferred range is 370 to 380 parts.

A preferred range for the silicon containing compound is 200 to 600 parts preferably 200 to 300 parts. A further preferred range for the silicon containing
15 compound is 450 to 550 parts. A still further preferred range is 470 to 530 parts. A yet still further preferred range is 480 to 500 parts.

A preferred range for the oil is 250 to 450 parts. A further preferred range for the oil is 300 to 400 parts. A still further preferred range for the oil is 350 to 390 parts. A yet still further preferred range for the oil is 370 to 380 parts.

20 The self curing composition preferably includes 10 to 50 parts of a biocide. The self curing composition further preferably includes 10 to 30 parts of the biocide. The composition is preferably mixed together in an aqueous solution.

The self curing composition is admixed with a base thermoplastic polymer in such a ratio so as to provide curing or crosslinking of the base thermoplastic polymer
25 under conditions of high humidity and/or low temperature.

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A preferred range for the base thermoplastic polymer is 50 to 150 parts. A further preferred range is 70 to 140 parts. A still further preferred range is 80 to 130 parts.

5 A preferred range for the self curing composition is 5 to 50 parts. A further preferred range is 10 to 40 parts. A still preferred range is 20 to 30 parts.

All parts for the admixture of the self curing composition and the base thermoplastic polymer are given in parts by volume.

10 A preferred ratio of the self curing composition to the base thermoplastic polymer is 1 to 15. A still preferred ratio is 1.5 to 13. A still further preferred ratio is 2 to 10.

EXAMPLES OF THE INVENTION

The present invention will now be illustrated with reference to the following example.

EXAMPLE 1

15 A biocide was added to water in a vessel to form an aqueous solution and then stirred so that the biocide was evenly distributed throughout the aqueous solution. A corn starch was then added to the aqueous solution by slow sprinkling at high speed and then followed by stirring at slow speed for approximately one hour.

20 In a separate formulation, sodium silico fluoride was pre-mixed with canola oil such that a smooth paste is formed. A further quantity of canola oil is mixed with the smooth paste until the paste is uniform in texture.

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The pre-mixed formulation of sodium silico fluoride and canola oil is then added to the vessel containing the aqueous solution of biocide and corn starch. The aqueous solution is then stirred at medium speed until a viscous liquid is formed.

5 The promoter composition is then added to a base material which in this example is a polychloroprene resin. The polychloroprene resin is an anionic resin which is acrylic modified and pigmented with silica flour and suitable iron oxides, titanium oxides and zinc oxides. The base material may also be an anionic bitumen emulsion.

10 The polymeric composition of the present invention is typically used as a single pack material for forming a waterproofing membrane. The viscous liquid is applied to a surface where the waterproofing composition self cures at a temperature of 5 to 35 degrees Celsius and at 98 per cent relative humidity. However, the polymeric composition may also be used in the form of a spray, a gel or as a brushable composition. After a period of up to 24 hours, the
15 polychloroprene base material has cured to form a waterproof elastomeric rubber product.

A first formulation of the composition used in the example is as follows:

- a) 15 to 30 parts of a biocide;
- b) 350 to 380 parts of a corn starch;
- 20 c) 480 to 520 parts of a sodium silico fluoride;
- d) 350 to 375 parts of canola oil.

The balance of the composition is made of water.

A second formulation of the composition used in the example is as follows:

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- a) 15 to 30 parts of a biocide;
- b) 350 to 380 parts of a corn starch;
- c) 200 to 300 parts of a sodium silico fluoride;
- d) 350 to 375 parts of canola oil.

5 The balance of the composition is made of water.

The pot life of the self curing composition is 30 to 60 minutes at 35 degrees Celsius and 5 to 6 hours at 20 degrees Celsius.

The cure / set times of the self curing composition were evaluated in the following apparatus. The apparatus provides adverse conditions of high relative humidity of 80 to 98 percent and elevated temperatures of 28 to 40 degrees Celsius. The apparatus has an insulated chest having an internal capacity of 40 litres and a removable insulated clip on lid. A thermostatically controlled immersion heater is provided in a sealed water bath within the inside of the chest. High relative humidity is achieved by use of an open water reservoir which contains warm or hot water depending on the conditions required. The lid of the insulated chest is fitted with a continuous read out thermohygrometer for the monitoring of the environment. Test panels are mounted in either horizontally or vertically in a rack so that there is no direct contact with any water in the bottom of the insulated chest. A circulating fan is optionally provided to provide air movement.

20 The cure time of the above example is as set out as follows for a coating applied to a dry surface and to a water saturated surface:

Temp/ Relative Humidity	Dry surface	Water saturated surface.
35 degrees C/ 98%	approx. 30 mins	approx. 4 hrs.

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20 degrees C/50 %

approx 15 mins

approx. 1.5 hrs

In Figure 1, there is shown a graph of temperature (in degrees C) versus relative humidity for polymeric compositions with and without the self curing composition of the present invention.

- 5 The parabolic curve as shown by the dash and dot line illustrates the temperature and relative humidity conditions of prior curing compositions.

The broken line with a series of dashes illustrates the temperature and relative humidity conditions of the present invention. As can be seen from figure 1, the area of gain is shown by the shaded area between the pair of lines.

- 10 In use, the self curing composition of the present invention is preferably used with polychloroprene type resins to form waterproof membranes. In waterproofing applications, the self curing composition will self cure within a predetermined time to form a cured or crosslinked elastomeric rubber product which is substantially waterproof. In particular, the self curing composition of the present invention will
- 15 self cure in conditions at high humidity and low temperature.

Throughout this specification, unless the context requires otherwise, the word "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

- 20 It is to be understood that the present invention should not be restricted to the particular embodiments or examples described above. Modifications and variations such as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.

CLAIMS

1. A self curing composition for a polymeric composition comprising
 - (a) a silicon containing compound or a salt with limited solubility,
 - (b) an oil, an olefine or a fatty acid; and
 - 5 (c) a starch, a carbohydrate, a polysaccharide, a cellulose or a gum.
2. A self curing composition according to claim 1 wherein the oil has a medium saponification number.
3. A self curing composition according to claim 2 wherein the oil is a naphthenic, process oil or a vegetable oil.
- 10 4. A self curing composition according to claim 3 wherein the vegetable oil is cottonseed, peanut, rapeseed, sunflower, canola oil , or safflower oil or a mixture of one or more of the aforesaid oils.
5. A self curing composition according to claim 1 wherein the starch is a cold water swellable and soluble starch.
- 15 6. A self curing composition according to claim 5 wherein the starch is in the form of a corn starch.
7. A self curing composition according to claim 1 wherein the silicon containing compound is a halogen containing compound.
8. A self curing composition according to claim 7 wherein the silicon
20 containing compound which contains halogen comprises fluorine containing and chlorine containing compounds.

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9. A self curing composition according to claim 8 wherein the halogen containing silicon compounds include alkali silico halides.
10. A self curing composition comprising
- (a) a thermoplastic polymer;
- 5 (b) a self curing composition comprising a silicon containing compound, an oil and a starch.
11. A self curing composition according to claim 10 wherein the thermoplastic polymer is a polychloroprene polymer, bituminous polymer, asphaltic polymer or any anionic emulsion of a thermoplastic polymer.
- 10 12. A self curing composition according to claim 11 wherein the polymers comprise acrylic resins, polyurethanes, Styrene/Butadiene/Rubber (SBR) resins, polyvinyl acetate resins, synthetic rubber resins and polyethylenes and polyvinyl chloride resins.
13. A self curing composition according to claim 10 wherein the self curing
15 polymeric composition is a controlled release self curing composition which operates such that curing of the polymer will occur after a predetermined time.
14. A self curing composition according to claim 13 wherein The predetermined time is in the range of half an hour to 8 hours.
15. A self curing composition according to claim 10 wherein the starch is
20 present in said self curing composition in the amount of 300 to 450 parts by weight.
16. A self curing composition according to claim 15 wherein the starch is present in the amount 320 to 420 parts by weight.

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17. A self curing composition according to claim 16 wherein the starch is present in the amount of 350 to 400 parts by weight.
18. A self curing composition according to claim 17 wherein the starch is present in the amount of 370 to 380 parts by weight.
- 5 19. A self curing composition according to claim 10 wherein the silicon containing compound is present in said self curing composition in the amount of 200 to 600 parts by weight.
20. A self curing composition according to claim 19 wherein the silicon containing compound is present in said self curing composition in the amount of
10 200 to 300 parts by weight.
21. A self curing composition according to claim 19 wherein the silicon containing compound is present in said self curing composition in the amount of 450 to 550 parts by weight.
22. A self curing composition according to claim 10 wherein the silicon
15 containing compound is sodium silico fluoride.
23. A self curing composition according to claim 10 wherein the oil is present in said self curing composition in the amount of 250 to 450 parts by weight.
24. A self curing composition according to claim 23 wherein the oil is present in said self curing composition in the amount of 300 to 400 parts by weight.
- 20 25. A self curing composition according to claim 24 wherein the oil is present in said self curing composition in the amount of 350 to 390 parts by weight.
26. A self curing composition according to claim 10 wherein said self curing composition comprises 10 to 50 parts of a biocide.

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27. A self curing composition according to claim 10 wherein said self curing composition comprises an amount of said thermoplastic polymer in the composition of 50 to 150 parts by weight and an amount of 5 to 50 parts by weight of said self curing composition.
- 5 28. A method of controlling the curing of a thermoplastic polymer comprising the steps of
- a) premixing a starch, an oil and a curing agent in an aqueous solution to form a coated curing agent;
 - b) adding the coated curing agent to the thermoplastic polymer;
- 10 such that thermoplastic polymer will be cured over an extended period of time.
29. A self curing thermoplastic polymeric composition according to claim 1 wherein said composition comprises a thermoplastic polymer:
30. A self curing composition according to claim 29 wherein the thermoplastic polymer is a polychloroprene polymer, bituminous polymer asphaltic polymer or
- 15 any anionic emulsion of a thermoplastic polymer.

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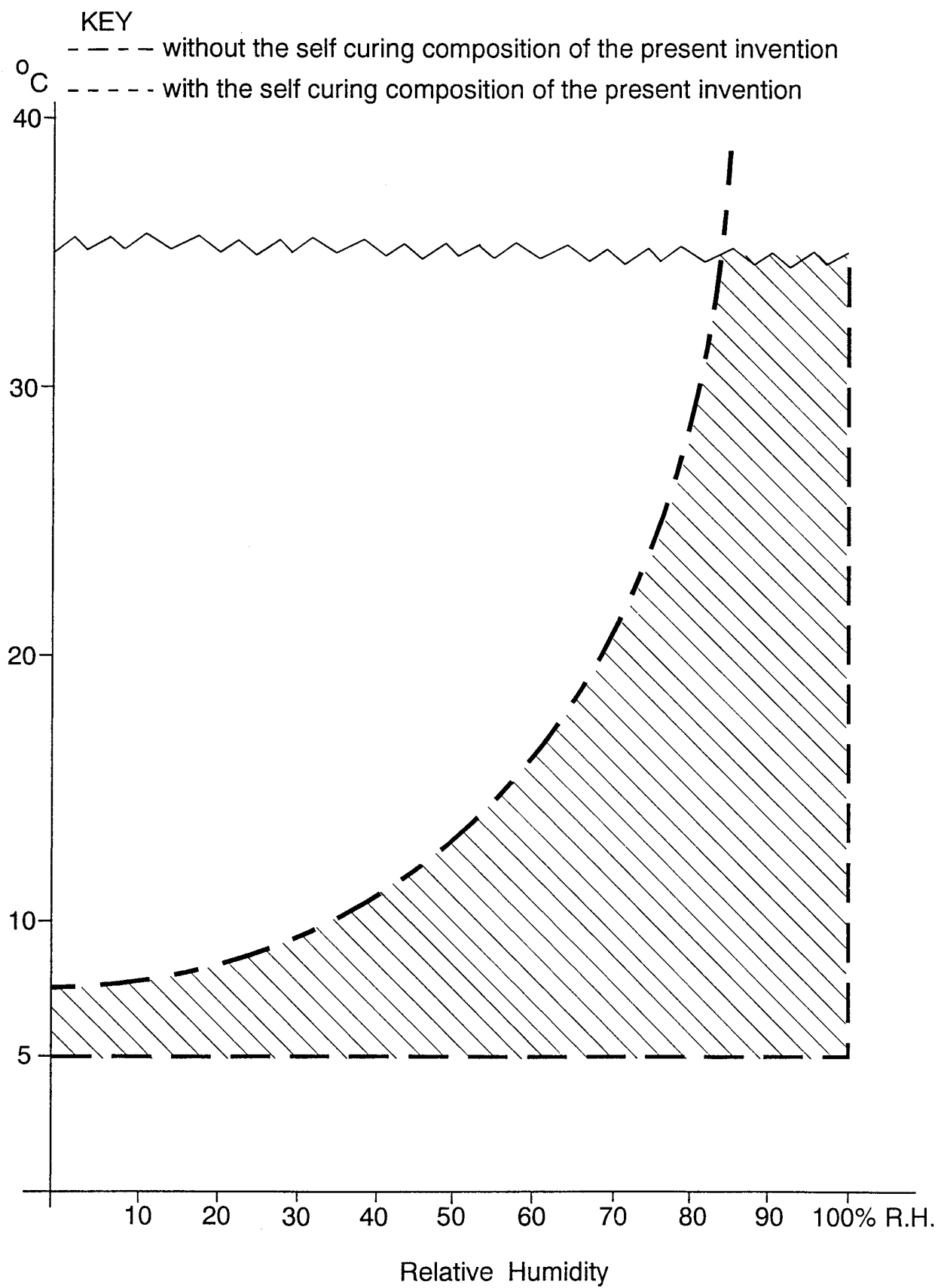


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.
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A. CLASSIFICATION OF SUBJECT MATTER												
Int Cl ⁶ : C08J 3/24; C08L 1/02, 3/02, 5/00, 91/00; C08K 5/01, 5/09, 5/10, 3/34, 9/04												
According to International Patent Classification (IPC) or to both national classification and IPC												
B. FIELDS SEARCHED												
Minimum documentation searched (classification system followed by classification symbols) IPC C08J 3/34; C08L 1/02, 3/02, 5/00, 91/00; C08K 5/01, 5/09, 5/10, 3/34, 9/04												
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT:[C08L91/00 OR C08K 5/01 OR 5/09 OR 5/10] AND [C08L 1/02 OR 3/02 OR 5/00] AND [C08K 3/34 OR 9/04] JAPIO: as above for WPAT												
C. DOCUMENTS CONSIDERED TO BE RELEVANT												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.										
A	US 5561177 A (Khaledi et al) 1 October 1996 entire document	1-30										
A	US 5026744 A (Callander) 25 June 1991 entire document	1-30										
A	US 4761442 A (Jenal) 2 August 1988 entire document	1-30										
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Date of the actual completion of the international search 3 September 1998		Date of mailing of the international search report 10 SEP 1998										
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C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4229333 A (Wolff et al) 21 October 1980 entire document	1-30
A	EP 455073 A (Aqualon Company) 6 November 1991 entire document	1-30
A	JP 06240038 A (Asahi Glass Co Ltd) 30 August 1994 Abstract	1-30
A	JP 63314276 A (Grace W.R. Co) 22 December 1988 abstract	1-30

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Information on patent family members

International Application No.

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Patent Document Cited in Search Report				Patent Family Member			
US	5026744	CA	2002032				
US	4761442	AU	37492/85	DK	5868/85	FI	855036
		IT	1203602	NO	855089	WO	8603764
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		FR	2321518	GB	1524077	IT	1045580
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